POROUS THIN FILM AND PROCESS FOR ANALYTE PRECONCENTRATION AND DETERMINATION

FIELD OF THE INVENTION

The present invention relates generally to materials and methods for analyte determination. More particularly, the invention relates to a porous thin film and process for preconcentration and determination of analytes in fluids and gases.

BACKGROUND OF THE INVENTION

Preconcentration of analytes has long been recognized as a way to enhance the sensitivity of selected analytical methods. Preconcentration increases the analyte concentration, and removes other potentially interfering constituents in a matrix, thereby making an assay more effective over a broader range of conditions. One recognized technique for direct multielemental analysis of solids is X-Ray Fluorescence (XRF). However, trace analysis of analytes in liquids by XRF has proven to be largely ineffective due to very poor detection limits for the analytes. Thus, other analytical techniques have proven more attractive for this type of analysis. Although a variety of ways have been proposed in the literature for improving XRF results for fluid samples, these methods have not been commercialized primarily because they do not provide a technically effective method to obtain the degree of preconcentration necessary from liquid samples in a stable, rapid and cost effective manner. Most solid phase sorptive materials fail to provide sufficient degrees of preconcentration, are heterogeneous, and have an incompatible physical form (uniformity, porosity, thickness, etc.) to enable direct XRF analysis. While preconcentration can be effected, e.g., by bulk solvent removal, solvent extraction, selective membranes, or selective capture by ion exchange resins, each of these approaches is labor intensive, and some of these methods also require significant quantities of laboratory reagents that can generate significant amounts of chemical waste. Various research teams have suggested that highly porous ceramic thin films could be useful for enhancing sensor performance. However, mesoporous thin films known in the art, whether spin-cast or dip-cast, have failed to demonstrate successful preconcentration of, e.g., ionic species in aqueous media simply because these films have not been shown to be hydrothermally stable. When immersed in a condensed aqueous phase, for example, spin-cast and dip-cast thin films delaminate, dissolve, or densify due to the high strain fields inherent in these films. Templated sol-gel approaches for making thin films introduce tremendous interfacial strain in the thin films during the curing process which can lead to film delamination, pore structure collapse, and film dissolution, all of which are detrimental to the use of these films for sensing/detection applications. The surfactant templating process also creates pores that tend to align parallel to the plane of the film and may not be accessible to solution-borne analytes. Surfactant templated sol-gel processes also tend to result in film structures that contain a dense, non-porous "skin", or capping layer, at the film interface, which can shut down diffusion into the porous films and negates the value of the high surface area porosity underneath. Other methods for making porous silica films include gluing silica powders to surfaces using adhesives or polymer melts. While this approach is simple and direct, it offers no direct control of film thickness, and can result in irregular film structures and film thicknesses. In addition, the adhesives can diffuse into the pores, blocking valuable surface area and active surface sites, which is detrimental to utilization of the porous films for analyte preconcentration for sensing/detection. Other methods of analyte preconcentration include the use of polymer thin films that have been doped with suitable ligands (either covalently attached to the polymer backbone, or simply percolated into the polymer film). Again, this approach is simple and direct, but it suffers from a number of drawbacks. For example, diffusion of analytes into a polymer thin film is slow, so preconcentration is time consuming. These polymer thin films are prone to solvent swelling, and even delamination, creating instability in the analytical results. Polymer thin films that include swellable organic matrices are also prone to fouling by organic constituents (e.g., proteins, humic acids and the like) which complicates the environmental sampling process and introduces error into the analytical output. Accordingly, new methods are needed that permit direct integration of preconcentration schemes into sampling/analysis protocols. Such protocols could simplify: 1) sampling procedures for extraction and preconcentration of analytes in fluids, 2) execution of the assays for determination of the analytes, and 3) long-term storage of the archived sample.

SUMMARY OF THE INVENTION

The invention in one aspect is a porous thin film that preconcentrates preselected analytes for analysis. The thin film includes fused silica particles that are generally uniformly distributed on a substrate and have a generally uniform thickness with an open interface. The particles have a generally open, multi-modal pore size distribution that is retained in the film with a surface area that is greater than about 200 m^2/g. Greater than about 50% of the surface area of the particles in the films is chemically accessible. The film can be functionalized with various ligands that selectively bind to preselected analytes that collect and concentrate the analytes in the film when contacted by the analytes in a fluid, e.g., in the vapor-phase, or in the liquid-phase. Ligands include, but are not limited to, e.g., thiols, carboxylates, sulfonates, phosphonates, amines, phosphines, ammonium salts, phosphonium salts, and like ligands. The films have a preferred thickness in range from about 0.1 μm to about 30 μm. More preferably, the films have a thickness in the range from about 0.3 μm to about 30 μm. Yet more preferably, the films have a thickness in the range from about 0.5 μm to about 50 μm. In various other embodiments, the films have a thickness in the range from about 0.1 μm to about 1 μm; or from about 1 μm to about 10 μm; or from about 10 μm to about 100 μm. The particles in the film have an open surface area of greater than about 90 percent. In the films, particle mesopores are of a size of from about 20' to about 200'. The films also include macropores in the calcined film external to the silicate particles with sizes that range from about 50 nm to about 50 microns. In various embodiments, the film can include preselected quantities of various preselected materials including, but not limited to, e.g., ceramics, metals, oxides, metal oxides, and combinations of these materials. In one embodiment, the uniform distribution of the film on the substrate is obtained by a process of screen-printing.

The invention, in another aspect, is a preconcentrator device that includes a porous thin film having a generally uniform thickness characterized by: fused silica particles generally uniformly distributed on a substrate. The particles of the preconcentrator have a generally open, multi-modal pore size distribution and the film has an open interface.

The invention in another aspect is a method for making a porous thin film that preconcentrates analytes for analysis. The method includes the steps of: distributing a slurry com-